



Evolution of the geothermal fluids at Los Azufres, Mexico, as traced by noble gas isotopes, $\delta^{18}\text{O}$, δD , $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$

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ARTICLE INFO

Article history:

Received 23 April 2012

Accepted 12 September 2012

Available online 21 September 2012

Keywords:

Noble gases
Strontium isotopes
Helium isotopes
Geothermal energy
Los Azufres
Araró
Mexico

ABSTRACT

Isotopes of noble gases, CO_2 , H_2O and Sr were measured in 10 geothermal wells and 8 hot springs, fumaroles and mud volcanoes at Los Azufres, the second most important geothermal field in Mexico. The aim of this study is to provide additional information on fluid circulation in the field and surrounding areas (Araró hot springs), as well as on physical processes such as boiling, steam separation and invasion of re-injected brines following over 25 years of geothermal fluid exploitation. Mantle helium dominates in fluids from the northern production zone of Marítaro, with measured $^3\text{He}/^4\text{He}$ ratios up to 7 Ra (where Ra is the atmospheric ratio of 1.386×10^{-6}). $^3\text{He}/^4\text{He}$ ratios are positively correlated with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and with δD and $\delta^{18}\text{O}$. These relationships suggest that Los Azufres fluids represent a mixing between primary magmatic ^3He -rich fluids and groundwater currently discharging at Araró hot springs and enriched in radiogenic ^4He acquired from Miocene andesites. Unusually high He ratios together with radiogenic Sr isotopic ratios suggest that thermal waters acquired mantle He from deep-seated parent magmas and radiogenic Sr possibly during their uprising through the metamorphic basement. $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of 366 to 429 measured in two wells indicate either mantle-derived argon or a radiogenic ^{40}Ar in situ component, suggesting the local presence of an older crustal fluid component in the northern part of the field. Ne, Kr and Xe are entirely of atmospheric origin, but processes of boiling, steam separation and re-injection of used brines have led to fractionation of their elemental abundances. Comparison with previous studies suggests that the boiling zone in the northern production zone is currently extending further north (Marítaro hot springs). In the southwestern productive zone, re-injected brines might account for more than 90% of the exploited fluids.

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1. Introduction

Los Azufres, located 200 km to the northwest of Mexico City, is the second most important geothermal field in the country after Cerro Prieto in the north (Fig. 1A). Most of the geothermal activity is concentrated in the southern portion of a large caldera within the Morelia–Acambay east–west rift zone (Fig. 1B), inside the Trans-Mexican Volcanic Belt (Pasquaré et al., 1988; Ferrari et al., 1991).

The Los Azufres geothermal field has been extensively studied in the past 30 years for its geological and tectonic features (Dobson and Mahood, 1985; Ferrari et al., 1991; Pradal and Robin, 1994), the geochemistry of the fluids (Nieva et al., 1987a; Gonzalez-Partida et al., 2000; Birkle et al., 2001; Gonzalez-Partida et al., 2003; Barragán et al., 2005; Gonzalez-Partida et al., 2005) and the evolution of the power capacity after 25 years of exploitation and re-injection of used brines

(Nieva et al., 1987b; Arellano et al., 2005; Barragán et al., 2005; Torres-Rodríguez et al., 2005). Despite the numerous studies carried out, noble gas data are scarce in Los Azufres (Prasolov et al., 1999) with only a few wells having been monitored for He and Ar to study the evolution of fluids as exploitation proceeded (Arriaga, 2002; Barragán et al., 2006). However, noble gases are excellent tracers of fluid evolution in general (e.g., Pinti and Marty, 1995; de Marsily et al., 2002; Patriarche et al., 2004; Morikawa et al., 2008) and those of geothermal areas in particular (e.g., Mazor and Truesdell, 1984; Kennedy et al., 1985; Smith and Kennedy, 1985; Mazor and Bosch, 1992; Kennedy and Truesdell, 1996; Goff et al., 2000; Saar et al., 2005; Kennedy and Van Soest, 2006; Ohwada et al., 2012). Noble gases definitively have the potential to provide information capable of enhancing exploitation of geothermal resources.

Noble gases present in geothermal fluids are from three potential sources: the mantle, the crust and the atmosphere. Geothermal fluids are typically meteoric freshwater which contains atmospheric noble gases (here denoted as ANG) dissolved during recharge

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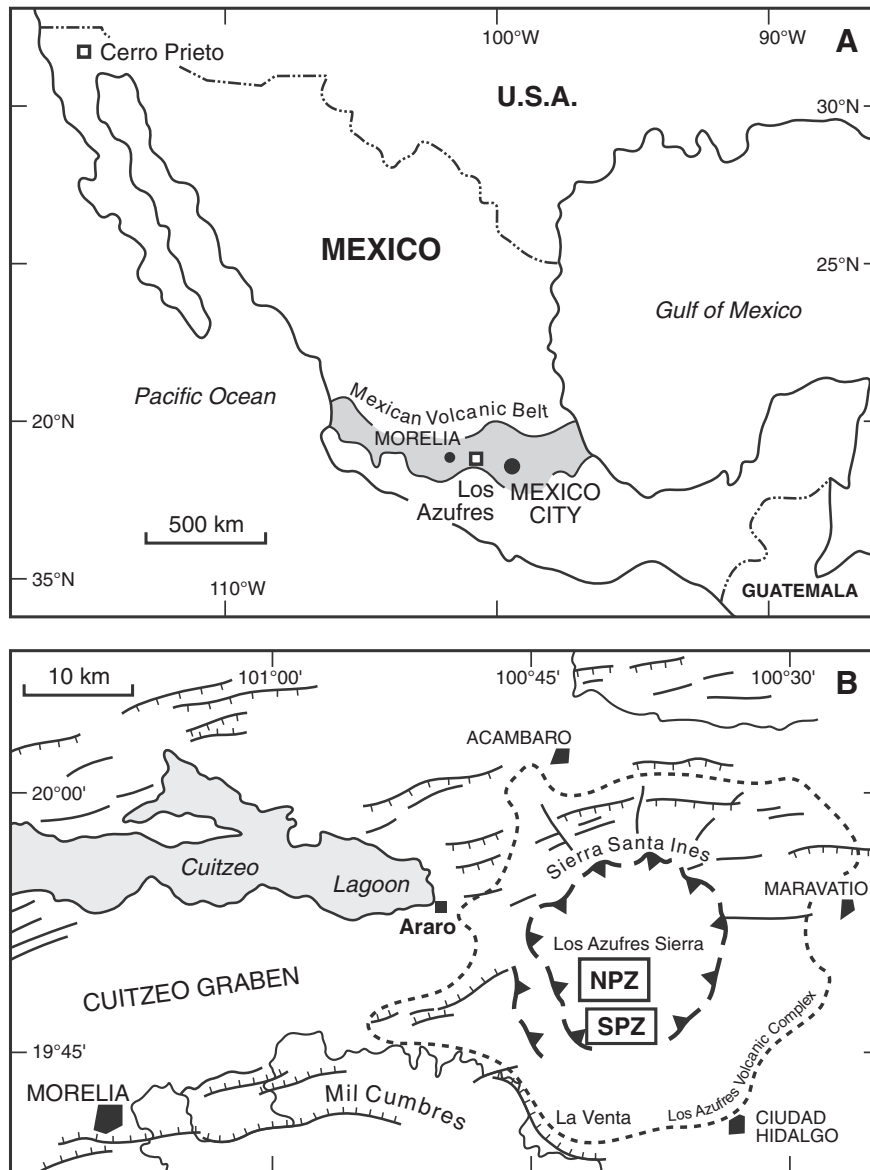


Fig. 1. (A) Simplified map of Mexico with the position of Los Azufres geothermal field within the Trans-Mexican Volcanic Belt. The location of Cerro Prieto is also indicated. (B) Simplified tectonic map of the Los Azufres Caldera and the E–W rift systems. The location of Araró hot springs on the border of Cuitzeo Lake is also indicated. NPZ and SPZ indicate the position of the northern production zone and the southern production zone of Los Azufres geothermal field, respectively.

following their dissolution in water (air saturated water conditions or ASW). This water subsequently evolves in the geothermal reservoir due to addition of radiogenic ^4He and possibly $^{40}\text{Ar}^*$ produced by decay of U, Th and K during prolonged high-temperature water–rock interactions (Kennedy and Van Soest, 2006). Most importantly, geothermal fluids contain a clear mantle ^3He component originating from the magmatic source that provides heat to the geothermal field (e.g., Mazor and Truesdell, 1984; Kennedy et al., 1985).

The occurrence of these three components in geothermal fluids is essential to obtain information on both the sources of thermal fluids and heat, the spatial distribution of fluid types, and subsurface fluid flow paths. Another important contribution of noble gases is to provide an understanding of the temporal evolution of geothermal systems, in particular when brines residual to steam flashing and power production are re-injected into or near the geothermal production reservoir. This is generally done either for environmental reasons or to increase the longevity of the geothermal field. However, re-injection of cooler used brines often has an effect opposite to that sought, leading to a decrease of power capacity of the geothermal reservoir. Therefore,

field management and production strategies need a reliable and sensitive tracer for monitoring the breakthrough of re-injected fluids. Noble gases can provide critical information on this front. Because noble gases have very low solubility in freshwater (Smith and Kennedy, 1983), particularly at high temperatures (Crovetto et al., 1982), phase separation (e.g. boiling) will generate a residual liquid that is strongly depleted in noble gases, and the noble gas composition will be fractionated relative to the original fluid composition. If production fluids can be shown to be a mixture of groundwater (ANG = ASW) and re-injected brine (ANG \ll ASW), accurate proportions of injected brine in the production steam can be easily calculated and monitored (Kennedy and Shuster, 2000).

To achieve such goals, a noble gas survey at Los Azufres geothermal field was carried out by measuring He, Ne, Ar, Kr and Xe in 10 deep wells (2 sampled and analyzed twice: AZ2 and AZ28) and 8 hot springs located within and outside of the Los Azufres caldera (Araró hot springs; Fig. 1B). Noble gas isotopes, stable isotopes of the water molecule ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$), the stable isotopic composition of CO_2 ($\delta^{18}\text{O}_{\text{CO}_2}$ and $\delta^{13}\text{C}_{\text{CO}_2}$) and the Sr isotopic composition ($^{87}\text{Sr}/^{86}\text{Sr}$), which is useful

to quantify water–rock interactions and mixing relationships in the field (Elderfield and Greaves, 1981; Graham, 1992), were measured. More specifically, the goal of this study was to couple noble gases with other water tracers in order to: (1) better identify water sources; (2) determine the spatial limits of the geothermal field, particularly to the north, where Araró hot springs have been alternatively interpreted as deriving from the Los Azufres fluid system (Tello and Quijano, 1983; Segovia et al., 2005) or being a completely independent hydrothermal system (Viggiano-Guerra and Gutiérrez-Negrín, 2005); and (3) determine how re-injection of residual brines (Fig. 2A,B) affects the power capacity of the field.

2. Geological background

Los Azufres is a typical high-enthalpy hydrothermal system with reservoir temperatures up to 320 °C, which is related to a collapsed volcanic caldera. It displays a dense fracturing system along three directions, NE–SW, E–W and NNW–SSE, from the oldest to the youngest, respectively (De la Cruz et al., 1982; Figs. 1B and 2A,B).

The 3000 meter-thick geothermal reservoir is hosted in a fractured, Upper Miocene to Pliocene basaltic andesite to dacite base complex called the *Mil Cumbres andesite* (Dobson and Mahood, 1985). K–Ar dating points to ages between 18.1 and 5.9 Ma for this unit (Dobson and Mahood, 1985). The *Mil Cumbres andesite* is overlain by andesitic lavas and basaltic andesites of the *Zinapécuaro andesite* unit dated at 0.87–0.85 Ma. The reservoir is sealed by a rhyolitic and rhyodacitic sequence of Pleistocene age that plays the role of cap-rock (Pradal and Robin, 1994). This sequence is composed of a series of fragmented lava flows and domes: (1) the basal *Aqua Fria rhyolite* dated between 1.6 and 0.84 Ma; (2) *San Andreas dacite* dated between 0.36 and 0.33 Ma; the *Yerbabuena rhyolite* dated between 0.3 and 0.14 Ma; (3) *Ciudad Hidalgo basalts* dated approximately at 0.15 Ma. Pradal and Robin (1994) report younger ages of 38 ka to 26 ka for the last rhyolitic ignimbrite. This suggests that the volcanic activity related to a voluminous differentiated magma body at shallow depth is not yet over, in particular in the southern area, in and around the resurgent zone occupied by the geothermal field (Pradal and Robin, 1994).

The field is divided into two distinct regions: Maritaro, in the north, and Tejamaniles, in the south (Figs. 1b and 2a,b). Two lithological units

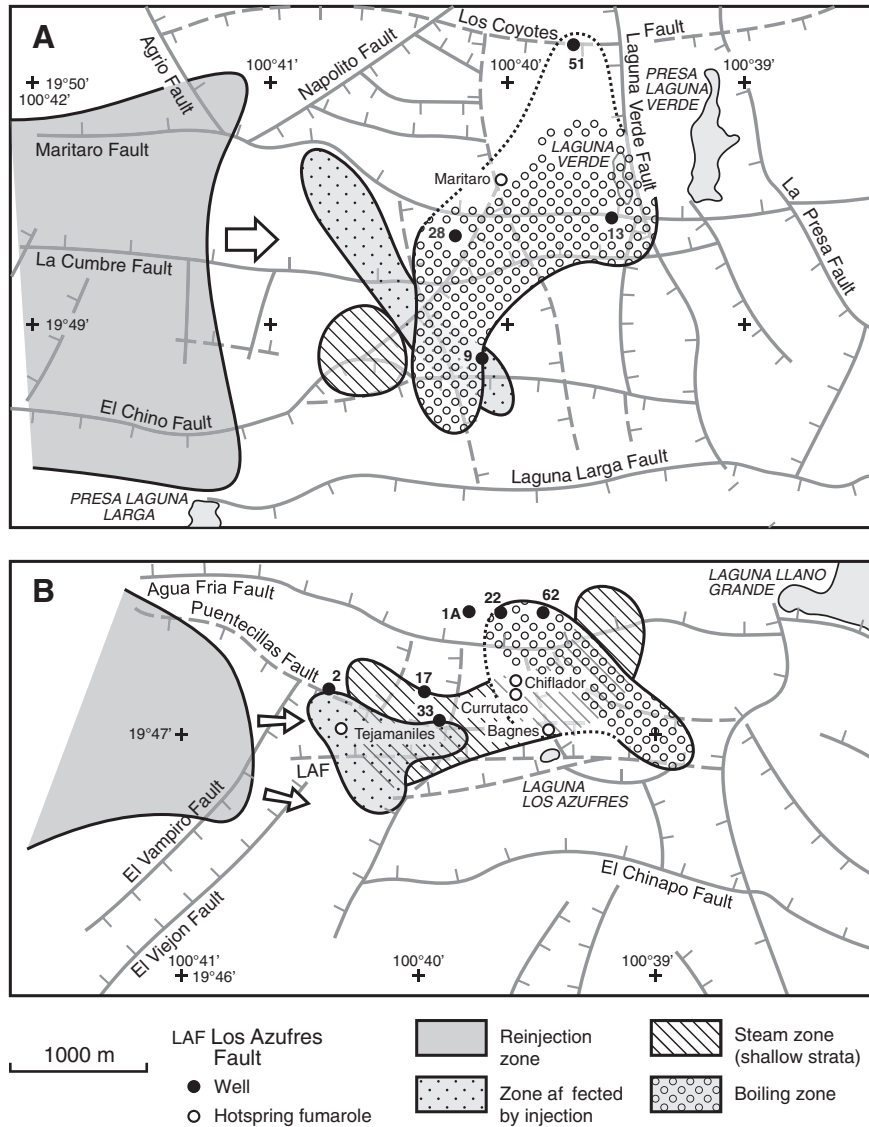


Fig. 2. (A) Simplified map of the Los Azufres northern production zone (NPZ) and (B) the southern production zone (SPZ). Main tectonic structures, sampled wells (closed circles) and hot springs (open circles) are indicated. The area of re-injection of the used brines, the productive area affected by re-injection, the boiling zone, and the steam-dominated zone as reported by Barragán et al. (2005) are also shown. Dashed contours indicate the extension of the boiling zone in the NPZ as inferred from fractionation patterns of noble gases measured in this study.

constitute the reservoir in the northern productive zone (NPZ hereafter; Fig. 2A): *Mil Cumbres andesites* hosting the reservoir and *Agua Fría rhyolite* that it is operating as a sealant cap. Fluids in the reservoir are of the NaCl type and thermodynamically are in the sub-cooled liquid region (Torres-Rodríguez et al., 2005). The reservoir in the southern productive zone (SPZ hereafter; Fig. 2B) presents the highest temperatures, with greater production in the field and is shallower than in the north. The reservoir consist of three lithological units: *Mil Cumbres andesites* hosting the reservoir, *Agua Fría rhyolite* that it is operating as a sealant cap and the *Tejamaniles dacite* that is the most recent volcanic unit which hosts most of the thermal springs (Torres-Rodríguez et al., 2005). Fluids in the southern reservoir are of NaCl type and thermodynamically are in three different regions: steam-dominated zone (2300 to 1900 m asl); liquid-dominated zone (1900 to 1200 m asl) and compressed liquid zone (1200 to 1300 m asl) (Torres-Rodríguez et al., 2005). Most of the productive wells have been drilled at the intersection of the three structural systems, NE–SW, E–W and NNW–SSE. Indeed, these areas are intensely fractured leading to greater hydraulic conductivity values and consequently, greater amounts of exploited fluid than in other areas.

The stable isotopic composition of water from wells and springs ($\delta^{18}\text{O}$, δD) indicates that waters are a mixing between “magmatic” and meteoric waters (Gonzalez-Partida et al., 2000; Birkle et al., 2001). Temporal changes in chemical constituents such as chloride, oxygen ($\delta^{18}\text{O}$) and deuterium (δD) isotopes have been analyzed in order to assess the impact of the exploitation on pristine geothermal fluids (Barragán et al., 2005). Re-injection of exploited brines is done at the western border of the productive zone (Fig. 2A,B) to maintain the reservoir pressure and to increase longevity of the field. Re-injection of brines causes steam boiling and separation that translates into an isotopic enrichment for N_2 , oxygen and hydrogen and high chloride contents, and minimum values for fluid enthalpies and reservoir temperatures in the southern zone of the field (Nieva et al., 1987a; Barragán et al., 2005).

3. Sampling locations and analytical methods

Sampling was carried out in two distinct periods, December 2007 and February 2009. Selection of sampling sites (Fig. 2A,B) was decided as follows:

- (1) Obtaining isotopic E–W transects from deep wells tapping into the active geothermal reservoir in both northern (AZ-9, AZ13, AZ28, AZ-51; Fig. 2A) and southern production zones (AZ1A, AZ2, AZ-17, AZ22, AZ-33, AZ-62; Fig. 2B) to assess the impact of re-injection of used brines;
- (2) Monitoring well-known thermal springs and fumaroles in both southern (Bagnes de Los Azufres, Tejamaniles, Currutaco, Chiflador; Fig. 2B) and northern (Marítaro; Fig. 2A) production zones for the above-mentioned reasons;
- (3) Determining isotopic patterns in the Araró thermal springs located north of Los Azufres, outside the caldera (Fig. 1B) to confirm or refute the hypothesis that these springs represent the discharge of the Los Azufres fluids (Segovia et al., 2005).

Gas samples were taken directly from the well through the steam/water separator. If the separation efficiency is 100%, the noble gas collected in the gas phase should represent the elemental and isotopic abundances of the liquid phase.

Noble gas samples were taken in standard refrigeration grade 3/8” Cu tubes ($\sim 14\text{ cm}^3$) sealed by stainless steel pinch-off clamps (Weiss, 1968) after gas was allowed to flow through for several minutes. Because of the high temperature of the steam phase reaching up to 300 °C, only metallic connections were used for sampling geothermal wells. A single copper tube was extended from the sampler to a NPT-type male connector on the steam separator conduit connected with a valve to regulate the pressure and gas flow through the tube.

Thermal springs and mud volcanoes were sampled using an inverse funnel cone to accumulate the gas and saturate the copper tubes with volcanic gases. Water samples for stable isotopes and radiogenic isotope analyses were taken using Nalgene® bottles saturated with fluids. The water was directly collected at the exit of the steam/water separator using a metallic container, waiting several minutes to cool down to an ambient temperature before transferring to the Nalgene® bottles.

Noble gases were measured at the Noble Gas Laboratory at the University of Michigan. Gas samples were attached to a vacuum extraction system and noble gases were quantitatively extracted for inletting into a MAP-215 mass spectrometer for isotopic analyses. Extracted gases were passed over a Ti sponge getter to remove reactive gases, and sequentially allowed to enter the MAP-215 mass spectrometer using a cryo-separator. The cryo-separator temperatures were set at 35, 65, 200, 215, and 270 K for analysis of He, Ne, Ar, Kr, and Xe, respectively. The ^4He , ^{20}Ne , and ^{40}Ar were measured using a Faraday detector while all other isotopes were measured using an electron multiplier in ion counting mode. During neon isotope analysis, a liquid N_2 cold trap was applied to minimize peak interferences and appropriate mass peaks were monitored to correct for interferences of $^{40}\text{Ar}^{++}$ and $\text{H}_2^{18}\text{O}^+$ on ^{20}Ne and CO_2^{++} on ^{22}Ne . The interference corrections for ^{20}Ne and ^{22}Ne were typically 1.1% and 0.17%, respectively. Before each sample analysis, a calibrated amount of air standard was analyzed following the same procedure of the sample measurement. Procedural blank corrections were applied to all measured peaks, but this correction was negligible. Isotopic abundances for each sample were normalized to the air standard after blank correction. Elemental abundances of ^4He , ^{22}Ne , ^{36}Ar , ^{84}Kr , and ^{132}Xe have typical uncertainties of 1.5%, 1.3%, 1.3%, 1.5%, and 2.2%, respectively and all uncertainties are at $\pm 1\sigma$ level.

^{18}O and ^2H isotopic analyses were conducted at the University of Waterloo in the Environmental Isotope Laboratory (EIL) using a VG micromass 903 Mass Spectrometer. Oxygen stable isotope measurements were performed on CO_2 by the $\text{CO}_2\text{--H}_2\text{O}$ equilibration method following Epstein and Mayeda (1953) and hydrogen stable isotope measurements were performed on H_2 gas using the Mn reduction method of Shouakar-Stash et al. (2000). Results are reported using the standard δ notation and values are expressed in parts per thousand. The standard used for calibration is the Vienna Standard Mean Ocean Water (V-SMOW). Measurement uncertainty for ^{18}O and ^2H is $\pm 0.2\%$ and $\pm 1\%$ respectively (Shouakar-Stash et al., 2007). Strontium isotope analyses were conducted at EIL, University of Waterloo, using a Triton Thermal Ionization Mass Spectrometer with a precision ranging between 0.0002 and 0.0003% (2σ).

CO_2 samples were collected in the same Cu tubes and using the same technique as that used for noble gases. For CO_2 stable isotope analyses, samples were transferred in pre-combusted quartz tubes using liquid nitrogen on a vacuum line (better than 5×10^{-2} mbar) and dried using an isopropyl alcohol–dry-ice bath ($-70\text{ }^\circ\text{C}$). After evacuation of incondensable gases, the tubes were sealed using a gas torch. Samples were then individually analyzed using a Micromass™ Isoprime™ universal triple collector IRMS in dual inlet mode. Oztech CO_2 was used as reference ($\delta^{13}\text{C} = -44.33\%$, $\delta_{18}\text{O} = -30.87\%$ vs. V-PDB). Results are reported relative to V-PDB (Vienna-Pee Dee Belemnite international standard) and analytical uncertainty is usually better than 0.05%.

4. Results

Table 1 reports the location, type of fluid collected, date of sampling together with ^4He , ^{20}Ne , ^{36}Ar , ^{84}Kr and ^{132}Xe abundances in the separated gas phase expressed as $\text{cm}^3\text{ STP}/\text{cm}^3_{\text{total gas}}$. Samples from wells AZ-9, AZ-17 and AZ-28b contained a condensate water phase and thus abundances were reported as $\text{cm}^3\text{ STP}/\text{cm}^3_{\text{H}_2\text{O}}$ (Table 1). Noble gas relative abundances are given in F-value notation (Table 1) in which measured abundances are normalized to the air abundance with ^{36}Ar as the reference isotope [e.g., $F(i) = (i/^{36}\text{Ar})_{\text{sample}} / (i/^{36}\text{Ar})_{\text{air}}$]. As defined,

Table 1
Location and noble gas elemental composition of geothermal wells and springs.

Locality	Type	Year sampling	Field zone	Phase sampled	⁴ He	²⁰ Ne	³⁶ Ar	⁸⁴ Kr	¹³² Xe	F(²⁰ Ne)	F(⁸⁴ Kr)	F(¹³² Xe)		
					(cm ³ STP/cm ³ gas) ^a					× 10 ⁻⁷	× 10 ⁻⁹	× 10 ⁻⁹	× 10 ⁻¹⁰	× 10 ⁻¹²
					× 10 ⁻⁷	× 10 ⁻⁹	× 10 ⁻⁹	× 10 ⁻¹⁰	× 10 ⁻¹²					
Araro east	Hot spring	2007	Cuitzeo	Condensate	1.73	416	836	153	561	0.95	0.88	0.90		
Araro west	Hot spring	2007	Cuitzeo	Condensate	4.30	196	410	107	497	0.91	1.26	1.63		
Araro north	Hot spring	2009	Cuitzeo	Condensate	28.41	3071	8080	2062	9956	0.73	1.23	1.65		
Maritaro 1	Mud volcano	2009	NPZ	Condensate	169.68	102	423	154	1327	0.46	1.76	4.21		
Maritaro2	Mud volcano	2009	NPZ	Dry	145.41	2894	7127	1698	7246	0.7	1.15	1.37		
Bagnes	Hot spring	2007	SPZ	Condensate	17.75	10.13	44.54	14.77	84.22	0.43	1.60	2.54		
Currutaco	Muddy spring	2007	SPZ	Condensate	9.16	6.99	20.33	7.46	44.34	0.66	1.78	2.93		
Tejamaniles	Hot spring	2007	SPZ	Condensate	1.26	357	708	136	498	0.96	0.93	0.95		
Chiflador	Fumarole	2007	SPZ	Condensate	13.41	1.37	6.43	3.54	35.40	0.41	2.66	7.39		
AZIA	Well	2009	SPZ	Condensate	n.d.									
AZ-2a	Well	2007	SPZ	Condensate	1.21	202	412	87.0	340	0.94	1.02	1.11		
AZ-2b	Well	2009	SPZ	Condensate	1.31	260	581	98.0	577	0.85	0.82	1.33		
AZ-9	Well	2009	NPZ	Water	0.57	0.60	2.40	0.67	4.07	0.48	1.36	2.28		
AZ-13	Well	2009	NPZ	Condensate	501.57	9.39	37.51	12.81	82.68	0.48	1.65	2.96		
AZ-17	Well	2009	SPZ	Water	86.63	1191	1746	300	1029	1.30	0.83	0.79		
AZ-22	Well	2009	SPZ	Condensate	151.15	51.55	164	39.5	179	0.60	1.16	1.47		
AZ-28a	Well	2007	NPZ	Condensate	0.18	0.12	0.15	0.06	0.33	1.57	1.96	2.94		
AZ-28b	Well	2009	NPZ	Water	0.29	0.26	0.57	0.19	1.54	0.89	1.64	3.64		
AZ-33	Well	2007	SPZ	Condensate	11.78	21.35	39.63	7.47	26.51	1.03	0.91	0.90		
AZ-51	Well	2009	NPZ	Condensate	271.46	26.38	145	54.33	391	0.35	1.81	3.63		
AZ-62	Well	2009	SPZ	Condensate	210.99	5.35	18.37	6.01	38.28	0.56	1.58	2.80		

Uncertainties (1 σ) on elemental abundances are 1.5% of the value (⁴He), 1.3% (²⁰Ne), 1.3% (³⁶Ar), 1.5% (⁸⁴Kr) and 2.2% (¹³²Xe).

Uncertainty (1 σ) on measured ³⁶Ar abundance of Maritaro 1 sample is 4.9% of its value.

Propagated uncertainties (1 σ) are 1.9% of F(²⁰Ne), 2.0% of F(⁸⁴Kr) and 2.6% of F(¹³²Xe) value, respectively.

^a Concentrations for samples containing a water phase (AZ9, AZ17, AZ28) are given in cm³ STP/g_{H2O}.

F-values are fractionation factors that provide a measure of enrichment or depletion relative to the atmospheric composition and can be useful fingerprints of boiling and gas depletion in the reservoir (e.g., Mazor and Bosch, 1992).

Table 2 reports the measured ³He/⁴He ratios (R) normalized to that of present-day atmosphere (Ra = 1.386 × 10⁻⁶; Ozima and Podosek, 1983) together with the neon (²⁰Ne/²²Ne and ²¹Ne/²²Ne) and argon (³⁸Ar/³⁶Ar and ⁴⁰Ar/³⁶Ar) isotopic ratios. The Kr and Xe isotopic compositions are completely atmospheric and are reported in the online data repository. Table 3 shows stable isotopes of the water molecule ($\delta^{18}\text{O}$, δD), the stable isotopes of the CO₂ molecule ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$) and Sr isotopic

ratios in water (⁸⁷Sr/⁸⁶Sr) measured in some hot springs and geothermal wells.

Fig. 3 shows the R/Ra values measured in the fluids of Los Azufres plotted against the ⁴He/²⁰Ne ratio, a useful indicator of air contamination. Regression analysis suggests that the He isotopic composition of Los Azufres fluids results from mixing between a pure air component (R/Ra = 1 and ⁴He/²⁰Ne = 0.318) and two mantle components. The first has an initial R/Ra of 6.62 while the second displays an R/Ra of 5.10, resulting from the addition of ~23% of radiogenic ⁴He to the system (Fig. 3). To remove the air component introduced into the system during sampling or at depth by re-injection of used brines (see Discus-

Table 2
He, Ne and Ar isotopic ratios.

Locality	R/Ra	±	⁴ He/ ²⁰ Ne	(R/Ra) _c	±	²⁰ Ne/ ²² Ne	±	²¹ Ne/ ²² Ne	±	³⁸ Ar/ ³⁶ Ar	±	⁴⁰ Ar/ ³⁶ Ar	±
Araro east	1.84	0.02	0.416	4.55	0.31	9.80	0.01	0.0287	0.0002	0.1876	0.0013	293.0	1.0
Araro west	4.24	0.11	2.198	4.79	0.11	9.84	0.05	0.0294	0.0002	0.1889	0.0011	293.9	1.2
Araro north	3.08	0.04	0.925	4.17	0.05	9.88	0.02	0.0290	0.0001	0.1863	0.0009	292.5	0.9
Maritaro 1	6.72	0.06	165.9	6.73	0.06	10.10	0.03	0.0291	0.0002	0.1867	0.0005	297.9	0.9
Maritaro2	6.65	0.07	5.025	7.03	0.07	9.67	0.02	0.0288	0.0002	0.1878	0.0008	298.2	1.1
Bagnes	5.96	0.14	175.2	5.97	0.14	10.05	0.06	0.0295	0.0002	0.1872	0.0011	299.1	1.4
Currutaco	6.02	0.18	131.1	6.03	0.18	10.37	0.05	0.0303	0.0002	0.1892	0.0011	306.9	1.2
Tejamaniles	1.49	0.02	0.353	–	–	9.81	0.01	0.0285	0.0001	0.1870	0.0012	293.1	1.0
Chiflador	6.62	0.04	979.9	6.62	0.04	10.08	0.13	0.0301	0.0003	0.1888	0.0013	309.0	5.7
AZ-2a	2.79	0.11	0.599	4.81	0.14	9.72	0.06	0.0288	0.0002	0.1879	0.0012	293.3	1.4
AZ-2b	2.63	0.03	0.504	5.43	0.15	9.75	0.02	0.0288	0.0002	0.1848	0.0013	298.4	1.4
AZ-9	6.27	0.07	95.2	6.28	0.07	10.22	0.07	0.0293	0.0002	0.1861	0.0008	297.2	1.1
AZ-13	6.19	0.05	5344	6.19	0.05	10.62	0.13	0.0295	0.0001	0.1868	0.0009	366.4	2.4
AZ-17	5.16	0.04	7.276	5.34	0.04	9.82	0.02	0.0288	0.0002	0.1866	0.0006	293.1	1.0
AZ-22	6.58	0.06	293.2	6.59	0.06	9.98	0.08	0.0288	0.0002	0.1825	0.0011	311.5	2.0
AZ-28a	6.48	0.21	145.5	6.49	0.21	10.51	0.08	0.0304	0.0002	0.1939	0.0029	312.3	2.6
AZ-28b	5.92	0.06	11.07	5.93	0.06	n.d.	–	0.0298	0.0003	n.d.	–	306.7	14.8
AZ-33	6.61	0.16	55.17	6.64	0.16	9.82	0.06	0.0293	0.0002	0.1870	0.0010	298.8	1.3
AZ-51	6.00	0.04	1029	6.00	0.04	10.14	0.06	0.0295	0.0001	0.1873	0.0006	315.3	1.3
AZ-62	5.42	0.05	3942	5.42	0.05	10.41	0.09	0.0304	0.0001	0.1836	0.0012	429.0	3.0

Experimental uncertainties on He, Ne and Ar isotopes are 1 σ .

Uncertainties on the helium isotopic ratios corrected of air contamination (R/Ra_c) have been calculated using relevant equations from Sano et al. (2006).

Table 3
Stable isotopes of water, CO₂ and Sr isotopic composition of springs/wells.

Locality	$\delta D_{(H_2O)}$ ‰	±	$\delta^{18}O_{(H_2O)}$ ‰	±	$\delta^{13}C_{(CO_2)}$ ‰	±	$\delta^{18}O_{(CO_2)}$ ‰	±	$^{87}Sr/^{86}Sr$ ‰	±
Araro north	-63.9	0.24	-5.6	0.07	-9.4	0.01	-13.9	0.01	0.70402	0.00004
Maritaro 1	n.d.	-	n.d.	-	-7.8	0.01	-7.1	0.01	n.d.	-
Maritaro 2	n.d.	-	n.d.	-	-7.5	0.02	-0.4	0.04	n.d.	-
Maritaro 3	-32.4	0.53	1.9	0.13	n.d.	-	n.d.	-	0.70486	0.00004
Currutaco	n.d.	-	n.d.	-	-6.6	0.00	-7.9	0.01	n.d.	-
AZ1A	-39.8	0.48	0.2	0.05	n.d.	-	n.d.	-	0.70565	0.00005
AZ-2a	n.d.	-	n.d.	-	-6.7	0.01	-12.4	0.01	n.d.	-
AZ-9	-52.5	0.48	-0.4	0.08	-6.9	0.12	-6.6	0.01	0.70458	0.00005
AZ-13	n.d.	-	n.d.	-	-7.2	0.01	-3.5	0.01	n.d.	-
AZ-17	n.d.	-	n.d.	-	n.d.	-	n.d.	-	n.d.	-
AZ-22	-54.8	0.12	-0.6	0.05	-7.2	0.03	-9.2	0.01	0.70424	0.00006
AZ-28a	-54.4	0.19	-1.0	0.06	-7.6	0.01	-5.6	0.01	0.70475	0.00004
AZ-33	n.d.	-	n.d.	-	-7.4	0.01	-3.6	0.01	n.d.	-
AZ-51	-58.3	0.07	-2.2	0.04	n.d.	n.d.	-3.3	0.01	0.70411	0.00004
AZ-62	-56.0	0.14	-0.8	0.04	n.d.	-	n.d.	-	0.70440	0.00004

sion section), $^3He/^4He$ ratios were corrected as follows (Craig et al., 1978):

$$(R/Ra)_c = [(R/Ra)_{meas} - r] / (1 - r) \quad (1)$$

$$r = \left(\frac{^4He/^{20}Ne}{Air} \right) / \left(\frac{^4He/^{20}Ne}{meas} \right) \quad (2)$$

where $(R/Ra)_c$ is the $^3He/^4He$ ratio normalized to the atmospheric value Ra and corrected for air contamination; $(R/Ra)_{meas}$ is the helium isotopic ratio measured in the sample; $(^4He/^{20}Ne)_{Air}$ is the atmospheric ratio (0.318; Ozima and Podosek, 1983), while $(^4He/^{20}Ne)_{meas}$ is the ratio measured in the gas sample. If the observed $^4He/^{20}Ne$ ratio is close to the atmospheric value, term r (Eq. (2)) nears unity and the correction becomes extremely sensitive to measurement uncertainties and therefore may be erroneous (as for Tejamanilles which shows a $^4He/^{20}Ne$ measured ratio of 0.353, close to that of air of 0.318; Table 2). To correctly evaluate the uncertainties on the calculated $(R/Ra)_c$, we used relevant equations described in Sano et al. (2006).

When corrected for the air addition, $(R/Ra)_c$ values range from 4.17 in Araró north hot spring to 7.03 in Maritaro mud volcanoes (Table 2). This ratio is slightly higher than that of the subcontinental lithospheric mantle (SCLM) He (~6.5 Ra; Dunai and Baur, 1995). Using a simple mixing equation between a local SCLM He component with a $R/Ra \sim 7$ and a purely radiogenic crustal component ($R/Ra = 0.02$), the calculated

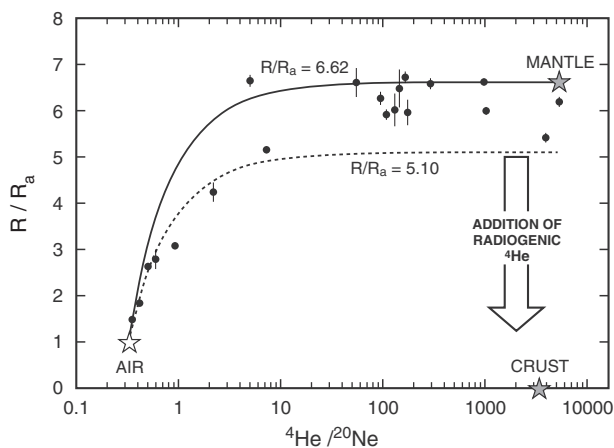


Fig. 3. $^3He/^4He$ ratio (R) normalized to that of the atmosphere (Ra) versus $^4He/^{20}Ne$ ratio. All data can be interpreted as a mixing between an atmospheric component ($R/Ra = 1$ and $^4He/^{20}Ne = 0.318$) and a He mantle rich component with R/Ra of 6.62 (representing the subcontinental lithospheric mantle, SCLM) diluted progressively by addition of radiogenic He (Crust).

percentage of mantle-derived helium in the Los Azufres fluids ranges from 100 to 69% of the total amount. Araró hot springs contain between 60 and 68% of mantle-derived He.

$^{20}Ne/^{22}Ne$ and $^{21}Ne/^{22}Ne$ isotopic ratios range from 9.67 ± 0.02 to 10.62 ± 0.13 and from 0.0285 ± 0.0001 to 0.0304 ± 0.0002 (1σ), respectively (Table 2). These values are close to the atmospheric values ($^{20}Ne/^{22}Ne = 9.80$ and $^{21}Ne/^{22}Ne = 0.0290$; Ozima and Podosek, 1983) or slightly mass fractionated by gaseous diffusion (Marty, 1984). The $^{38}Ar/^{36}Ar$ and $^{40}Ar/^{36}Ar$ isotopic ratios are also atmospheric within uncertainties or slightly mass fractionated by gaseous diffusion except for the $^{40}Ar/^{36}Ar$ ratios measured in wells AZ-62 ($^{40}Ar/^{36}Ar = 429.0 \pm 0.3$) and AZ-13 ($^{40}Ar/^{36}Ar = 366.4 \pm 2.4$). These values cannot be explained by kinetic fractionation during batch degassing. Because boiling and steam separation at depth (see Discussion section and Fig. 7A,B) caused elemental fractionation of noble gases, we could speculate that isotopic fractionation also occurred. However, there is no correlation between $F(i/^{36}Ar)$ and Ar isotopic values that could support such a hypothesis. Thus we assume that the high Ar isotopic ratios are genuine and reflect a source other than the atmospheric one.

5. Discussion

5.1. He, H, O and Sr isotopes: tracing the heat source and fluid circulation in the field

$(R/Ra)_c$ values measured in Los Azufres are among the highest measured in western North America geothermal fields (Fig. 4) and are within the range of those measured at the Cerro Prieto field in northern Mexico. The high $(R/Ra)_c$ values measured at Los Azufres provide strong evidence for an active shallow magma system beneath the field. The highest mantle helium percentage is found in mud volcanoes and fumaroles of Maritaro hot springs in the NPZ ($[R/Ra]_c = 7.03$; Table 2). This is in agreement with the observed high mineralization (Birkle et al., 2001) and very high δD (-32.4%) and $\delta^{18}O$ ($+1.9\%$) values (this study) measured in these springs, which suggests direct rise of “pristine” geothermal liquid and vapor to the surface. Fluids extracted from wells AZ13 and AZ51, both located in the northern production zone, show $^{40}Ar/^{36}Ar$ ratios of 366.4 ± 2.4 and 429.0 ± 0.3 , respectively. The excess of ^{40}Ar might be related to either a mantle or an in situ radiogenic component. Because the presence of a clear Ne mantle signature cannot be identified for these wells (all Ne isotopic ratios greater than the atmospheric value plot on a mass fractionation line for a residual gas phase) and because a correlation with $(R/Ra)_c$ is not observed, it is not possible at this stage to conclude whether or not part or all of this ^{40}Ar has a mantle origin. On the other hand, if these excesses are related to crustal $^{40}Ar^*$, the existence of older fluids in the northern part of the field is likely.

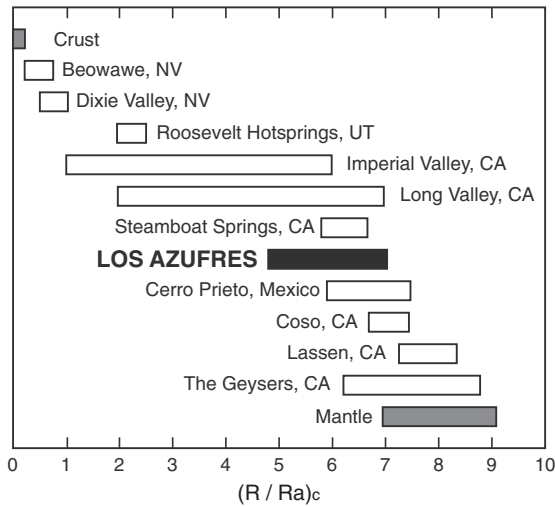


Fig. 4. Air-corrected helium isotopic ratios ($[R/Ra]_c$) measured in Los Azufres (this study), Cerro Prieto and several other geothermal fields in western USA. Mantle ($R/Ra = 8 \pm 1$) and crustal ($R/Ra = 0.02$) end-members are also indicated. Intermediate values represent either mixtures of these two end-members or magma aging effect. Relatively high R/Ra values measured in Los Azufres suggest that the heat source (magma) was emplaced recently, and that fluids should have a relatively short residence time in the system, resulting in low accumulation of radiogenic ^4He (aging effect). Figure modified from Kennedy and Van Soest (2006). Detailed bibliographic references are given in Kennedy and Van Soest (2006).

The lowest $(R/Ra)_c$ values measured in this study, between 4.17 and 4.79 (Table 2) are from the Araró hot springs located outside the Los Azufres caldera complex (Fig. 1B). These springs are thought to be representative of the Los Azufres fluid discharge (Segovia et al., 2005). Atmospheric corrected $(R/Ra)_c$ low values can only be explained by the addition of radiogenic ^4He . This could be produced by (1) old, stagnant fluids that accumulated ^4He produced in the reservoir rocks over time; or (2) freshwater exchanging ^4He with an older volcanic sequence that had the time to lower its initial mantle value due to internal production of ^4He (i.e., reservoir “aging” effect; e.g., Torgersen and Jenkins, 1982). $\delta^{18}\text{O}$, δD , and Sr isotopes can be helpful to assess which one of these hypotheses might be responsible for the lowest observed $(R/Ra)_c$ values.

The δD vs. $\delta^{18}\text{O}$ plot (Fig. 5) clearly indicates that geothermal fluids of Los Azufres are a mix between recent meteoric water and “andesitic water” (Giggenbach, 1992) and possibly with “primary magmatic water” (Sheppard and Epstein, 1970). Here we define “andesitic water” or “primary magmatic water” as the water that equilibrated with the magma body that furnished the mantle helium (and likely the heat) to the Los Azufres Geothermal field. Araró hot springs represent the most “meteoric” pole in the δD vs. $\delta^{18}\text{O}$ plot (Fig. 5) among the Los Azufres fluids. Thus, it is likely that Araró hot springs are originally meteoric waters that subsequently flowed through volcanic rocks sufficiently old to have lowered their initial mantle $^3\text{He}/^4\text{He}$ ratio by accumulation of in situ produced ^4He . These volcanic rocks could be the Miocene andesite that fills the caldera of Los Azufres (Fig. 1B).

This hypothesis is further supported by a direct relationship between $(R/Ra)_c$ values and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Fig. 6). The plotted values suggest a mixing between two end-members. The first end-member has a low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of ≤ 0.7040 and possibly a $^3\text{He}/^4\text{He}$ ratio of $\leq 5\text{Ra}$ (Fig. 6). The second end-member is enriched in mantle He ($R/Ra = 7.0$) and shows a slightly radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (0.7049) compared to the expected mantle value as measured in MORBs (≤ 0.7030). This relation is peculiar and the origin of both end-member fluids needs to be discussed in detail as it impacts the interpretation of fluid circulation in Los Azufres and the origin of the heat source of the field.

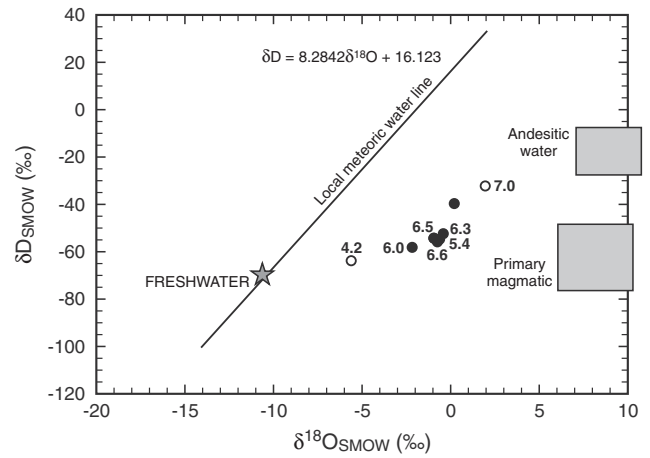


Fig. 5. Plot of δD vs. $\delta^{18}\text{O}$ of Los Azufres geothermal wells (closed circles) and hot springs (open circles). The local meteoric water line (LMWL) is calculated from Bowen (2011). Isotopic composition of recharge water is from Birkle et al. (2001). The field labeled “primary magmatic water” represents the isotopic compositions of water in equilibrium with unaltered plutonic formations as defined by Sheppard and Epstein (1970). The field “andesitic water” represents the isotopic composition of recycled seawater that enters the subduction system in the form of porewater, or as hydration water in clay minerals of accumulated marine sediments and is carried to the source region of arc magmas on top of the subducting slab (Giggenbach, 1992). Indicated values are the helium isotopic composition corrected for air contamination ($[R/Ra]_c$) except for well AZ1 for which noble gas analyses were not performed.

Based on $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured in well cores at Los Azufres, the first end-member could be andesitic volcanic units ($^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7038 ± 0.003 ; Verma et al., 2005) filling the Los Azufres caldera and which constitute the geothermal reservoir at depth. Because the andesitic units are 18.1 to 5.9 Ma old (Dobson and Mahood, 1985), they were not capable of retaining high R/Ra values due to their low helium concentrations and post-eruptive production of radiogenic ^4He . As fluids circulate through and equilibrate with the andesite, meteoric water might have acquired radiogenic ^4He which reflects the water–rock interaction process and rock composition integrated over the flow path of the fluid (e.g., Torgersen and Jenkins, 1982; Kennedy and Van Soest, 2006).

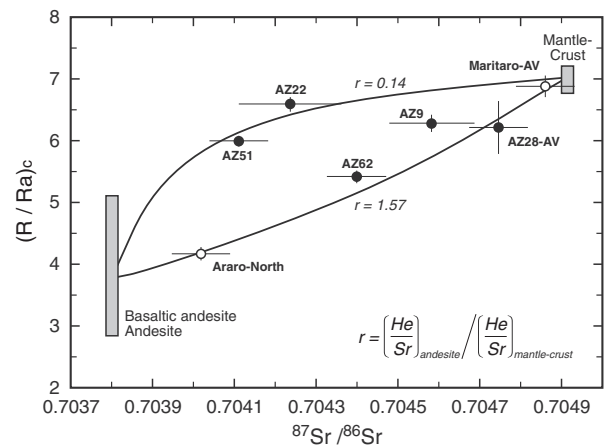


Fig. 6. $(R/Ra)_c$ values vs. the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios measured in geothermal wells (closed circles) and hot springs (open circles). $(R/Ra)_c$ duplicate data for Maritaro and AZ28 were averaged (labeled AV in the plot) and the uncertainties propagated. Data points roughly line up on a mixing trend between an He mantle-rich ($^3\text{He}/^4\text{He} \geq 7\text{Ra}$) and radiogenic Sr end-member ($^{87}\text{Sr}/^{86}\text{Sr} \geq 0.7049$) and a less radiogenic Sr ($^{87}\text{Sr}/^{86}\text{Sr} \leq 0.7038$) end-member here identified in the Miocene andesite, sufficiently aged to have lowered its initial mantle $^3\text{He}/^4\text{He}$ ratio by accumulation of radiogenic ^4He . Possible mixing hyperbolae between the two end-members are reported together with the calculated curvature factor “r”.

The time-dependent change in the helium isotopic composition of andesite due to addition of radiogenic ^4He is given by (Kennedy and Van Soest, 2006):

$$\left(\frac{^3\text{He}}{^4\text{He}}\right)_t = \left(\frac{^3\text{He}}{^4\text{He}}\right)_0 \cdot \left[\frac{1}{1 + [^4\text{He}]_t / [^4\text{He}]_0} \right] \quad (3)$$

where subscripts 't' and '0' refer to present-day and initial He concentrations and ratios, respectively. The time-dependent ^4He concentration is given by:

$$[^4\text{He}]_t = [^{238}\text{U}] \cdot t \cdot \left\{ 1.207 \times 10^{-7} + 2.797 \times 10^{-8} \cdot \left(\frac{^{232}\text{Th}}{^{238}\text{U}} \right) \right\} \quad (4)$$

where ^{238}U and ^{232}Th concentrations are in grams [U]/grams_{rock} and the ^4He concentrations are in cm^3 STP/g (Kennedy and Van Soest, 2006). We assume an initial ^4He concentration in basaltic andesites of 3.5 to $9.4 \times 10^{-6} \text{cm}^3$ STP/g (e.g., Hilton et al., 1993), an initial SCLM R/Ra ratio of 7, an average U and Th contents of 2 ppm and 4 ppm in andesite (Condie, 1993), and eruption ages between 18.1 and 5.9 Ma for the *Mil Cumbres* andesite formation (Dobson and Mahood, 1985). The resulting R/Ra ratio is of 4.01 ± 1.16 Ra, which is compatible with the helium isotopic composition measured in the Araró groundwaters (Fig. 6).

The second end-member of Fig. 6, characterized by high He mantle contents and radiogenic Sr, is unusual. This implies that the parent magma either had those high Sr isotope ratios together with mantle He, or during differentiation parent magmas assimilated crustal material with elevated Sr isotope ratios. The former hypothesis seems unlikely given that more primitive andesitic magmas have lower Sr isotope ratios (Fig. 6), so that would point to assimilation of crustal material. However, assimilation of crustal material would tend also to lower the He isotopic ratio by the addition of radiogenic ^4He (Marty et al., 1994).

Interestingly, the rhyolitic caldera of Long Valley, CA seems to be a case analogous to Los Azufres. Goff et al. (1991) measured very high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7078–0.7080 in thermal waters of the Long Valley caldera, where Welhan et al. (1988), Sorey et al. (1993) and Hilton (1996) have measured He isotopic ratios as high as 6.7 Ra. Goff et al. (1991) interpreted these radiogenic Sr isotopic ratios as having been derived by leaching of metamorphic units of the basement by uprising thermal waters. The high He isotopic ratios point to a pure mantle He source located deep beneath Long Valley caldera (e.g., Welhan et al., 1988; Sorey, 1985). We could speculate that in Los Azufres the mantle He component comes from deeper "primitive" parent magmas below the caldera. Mantle He-rich thermal waters acquired radiogenic Sr during their uprising through the basement. In Fig. 6 two mixing hyperbolas are reported to account for the observed He and Sr isotopic variability. For the andesitic end-member, we assume a Sr content of 300 ppm (Condie, 1993), a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7038 (Verma et al., 2005) and a $^3\text{He}/^4\text{He}$ ratio of 4 Ra (this study). The second end-member, here designated as "Mantle-Crust" (Fig. 6) has a Sr content of 350 ppm, equal to that of the continental crust (Taylor and McLennan, 1995), a minimum $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7049 (this study) and a $^3\text{He}/^4\text{He}$ ratio of 7 Ra (this study). Fixing the ^4He content in the mantle parent magmas to $6.7 \times 10^{-6} \text{cm}^3$ STP/g (Torgersen et al., 1995) leads to a ^4He content in andesite would vary between 1.5 and 0.1 times that of the mantle parent magmas, which is compatible with values measured in andesite (e.g., Hilton et al., 1993). Thus mixing of these two hypothetical sources is a viable process for explaining the He and Sr isotopic variability observed in the Los Azufres fluids.

If the magmatic sources providing mantle He to Los Azufres provide also heat, then the hypothesis of Pradal and Robin (1994) indicating the last rhyo-dacitic episode as the heat source of the field seems unlikely. Indeed, it would be inconceivable that these highly differentiated magmas would contain high mantle He. Both mantle

He and heat are likely provided by deeper located parental magmas beneath Los Azufres.

5.2. Elemental fractionation of noble gases during boiling, steam separation and injectate mixing

Re-injection of used brines into the geothermal reservoir can cause boiling, steam separation and a progressive decrease in the amount of liquid phase produced by the wells. In Los Azufres, re-injection of a condensed steam–water–air mixture (injectate) started in 1982. In 2000, the ratio between injected and produced fluids was around 50% (Barragán et al., 2005). Reservoir boiling and mixing of reservoir fluids with cooler fluids were the most important processes identified in 2000 by using stable isotopes as tracers of waste fluid re-injection (Barragán et al., 2005). The southern zone was the most affected by boiling processes and, in particular, by invasion of cooler waters (AZ2 and AZ33 wells). The northern zone was much less affected because of the poor fracture interconnectivity of the reservoir, which prevented invasion of large amounts of waste fluids (Barragán et al., 2005).

Noble gases, sampled almost ten years (2007 and 2009, this study) after the sampling campaign carried out by Barragan and colleagues in 2000 can be helpful in assessing present conditions of the geothermal reservoir. Indeed, noble gas elemental compositions are very sensitive to physical changes in the reservoir caused by fluid exploitation or waste fluid re-injection, and are easily fractionated compared to their equilibrium solubility concentrations (Mazor and Truesdell, 1984; Mazor and Bosch, 1992).

Fig. 7A shows $F(^{20}\text{Ne})$ versus $F(^{132}\text{Xe})$ values measured in both geothermal wells (closed circles) and hot springs and fumaroles (open circles). Fig. 7B shows $F(^{84}\text{Kr})$ versus $F(^{132}\text{Xe})$ values. $F(i)$ values for the atmosphere (= 1), air saturated water (ASW) at 10 °C and air saturated geothermal water (ASGW) at reservoir temperatures of 200 °C (the lowest value estimated at Araró; Segovia et al., 2005) and at 300 °C (average geothermal reservoir temperature at the production zones; Barragán et al., 2005) are also indicated. Solubility data from Crovetto et al. (1982) were used to compute boiling and steam phase separation processes.

Most of the samples depart from the expected ASGW elemental compositions (Fig. 7A,B) and two processes could explain this phenomenon: a) boiling and subsequent steam separation at depth (Fig. 7A,B); and b) mixing with injectate (Fig. 8A,B). During boiling and steam separation, the residual liquid phase will retain the more soluble, heavier noble gases (Kr and Xe compared to Ar) than the less soluble lighter noble gases (Ne compared to Ar). The escaped vapor phase will contain lighter noble gases (Ne) rather than heavier less soluble ones (Kr and Xe). This can be modeled as a Rayleigh distillation process, if we assume that the vapor phase is continuously removed from the system. In the residual liquid, this process is governed by the equation (e.g., Ma et al., 2009):

$$\left(\frac{i}{^{36}\text{Ar}}\right)_w = \left(\frac{i}{^{36}\text{Ar}}\right)_{\text{ASGW}} \cdot f^{\left(\frac{k_w^i}{k_w^{\text{Ar}}} - 1\right)} \quad (5)$$

where $f_{^{36}\text{Ar}}$ is the fraction of ^{36}Ar remaining in the residual water following boiling and steam separation. In the newly created steam phase, fractionation of noble gases will be governed by the equation (e.g., Matsumoto et al., 2004):

$$\left(\frac{i}{^{36}\text{Ar}}\right)_w = \left(\frac{i}{^{36}\text{Ar}}\right)_{\text{ASGW}} \cdot \frac{1 - f^{\left(\frac{k_w^i}{k_w^{\text{Ar}}}\right)}}{1 - f} \quad (6)$$

In Fig. 7B we simulated the boiling and steam separation effects starting from an ASGW calculated at reservoir temperatures of 200 and 300 °C. Boiling curves for the residual fluid, after steam separation, were simulated for an ASGW at 200 °C and subsequent boiling at the

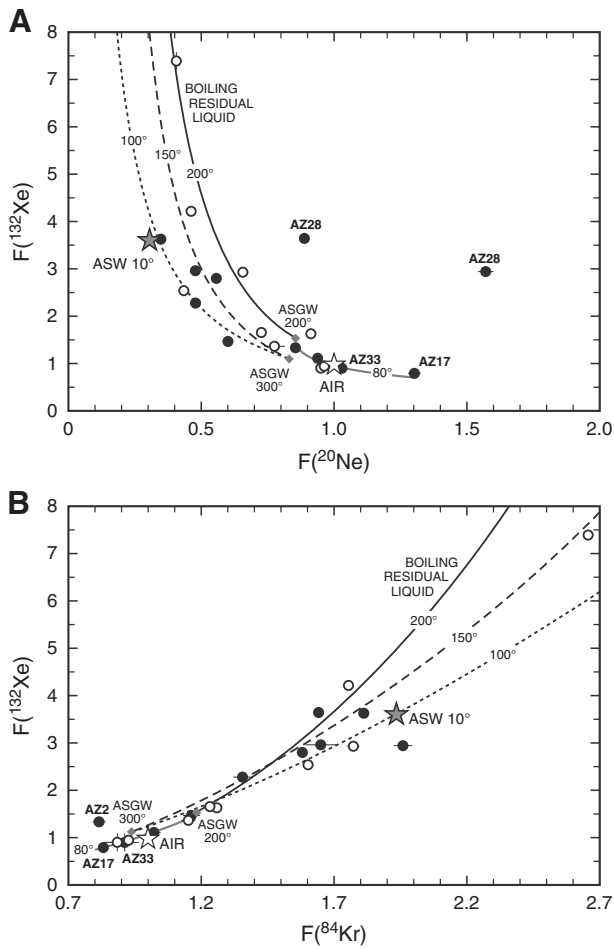


Fig. 7. (A) $F(^{20}\text{Ne})$ vs. $F(^{132}\text{Xe})$ ratios; and (B) $F(^{84}\text{Kr})$ vs. $F(^{132}\text{Xe})$ ratios measured in geothermal wells (closed circles) and hot springs (open circles). Diamonds labeled ASGW are for air saturated geothermal water and represent initial noble gas composition at depth at different temperatures. For reference, air initial composition is 1. Shown simulated curves are for an initial ASGW of 200 °C followed by subsequent boiling and steam separation at constant temperature, in addition to an initial ASGW at 300 °C followed by boiling and steam separation at lower temperatures of 150, 100 and 80 °C.

same temperature, and for an ASGW at 300 °C and boiling processes produced at lower temperatures of 150 and 100 °C. The boiling curve for the separated steam phase was simulated from an initial ASGW composition at 200 °C and steam separation at 80 °C. These simulations reproduce the elemental fractionation pattern measured in the hot springs and geothermal wells of Los Azufres and Araró (Fig. 7A,B).

Most of the $F(^{132}\text{Xe})$, $F(^{84}\text{Kr})$ and $F(^{20}\text{Ne})$ data plot close to the simulated distillation curves for a residual liquid after steam separation (Fig. 7A,B), except for geothermal wells AZ17 and AZ33, which show $F(i)$ values compatible with a sampled steam phase. Geothermal well AZ28 duplicate data show $F(i)$ values compatible with either a residual liquid and a separated steam phase. It is worth noting that AZ28a sampled phase is condensate gas while AZ28b phase is water (Table 3). It is possible that different efficiencies in the steam/liquid separator at the well head may cause different fractionation patterns in the collected phase for the same well over time. However inefficient gas/liquid separation from wellheads cannot explain the complete elemental fractionations observed in the field. Indeed, if we were collecting a gas phase only partially degassed from a residual liquid after steam separation, then we should observe scattered elemental ratios departing from the residual liquid curve towards lighter noble gas compositions, and this is not observed (Fig. 7A,B). AZ2 also shows $F(^{84}\text{Kr})$ and $F(^{132}\text{Xe})$ values that could possibly be compatible

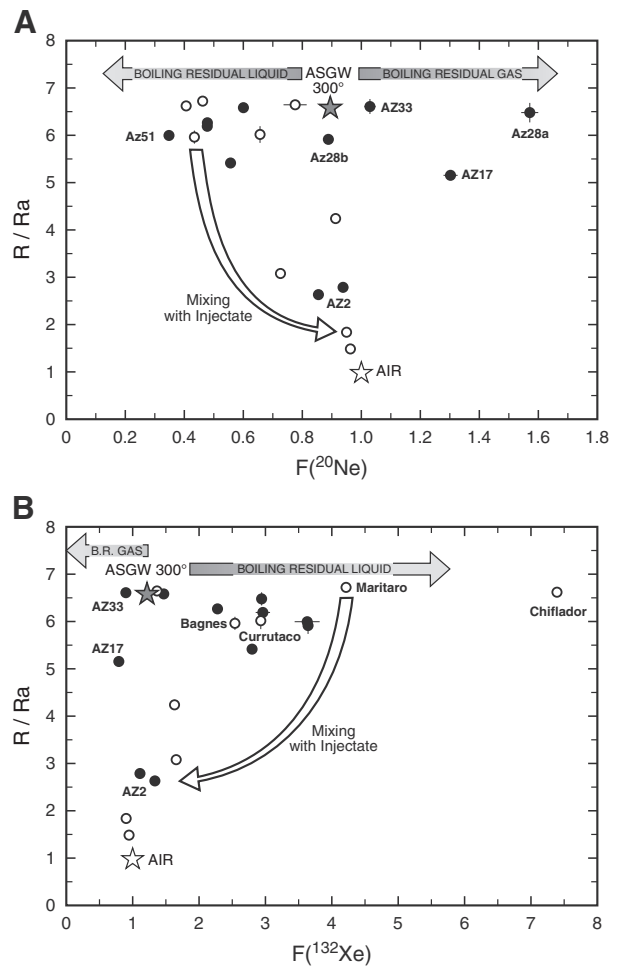


Fig. 8. (A) $F(^{20}\text{Ne})$ ratios and (B) $F(^{132}\text{Xe})$ ratios plotted vs. the helium isotopic compositions not corrected for air contamination (R/Ra). The isotopic variations of helium and elemental abundances of atmospheric noble gases can be explained by boiling and steam separation followed by massive air addition. Although some air addition in hot springs is likely due to air contamination, excess air in AZ2 appears to be ubiquitous in the well and unrelated to air contamination.

with a separated steam phase (Fig. 7B), but in reality, these values reflect a strong level of air contamination as shown in Fig. 8A,B.

From Fig. 7A,B it is apparent that changes in reservoir conditions took place since the study by Barragán et al. (2005) based on data sampled in 2000. Indeed, together with ambiguous well AZ28 in the northern zone, the most fractionated elemental abundances of noble gases were observed in well AZ51 and in one Maritaro hot spring (Fig. 8A, B). In 2000, both Maritaro and AZ51 were located outside of the zone affected by boiling (Fig. 2A). Our data suggest that this zone extends further to the north at present (Fig. 2A).

In the southern zone, the boiling zone, that in year 2000 covered (Fig. 2B) the area where AZ22 and AZ62 are located, should be extended to the west to include Currutaco, Chiflador and Bagnes hot springs, all showing elemental fractionation compatible with boiling at depth (Fig. 7A,B). AZ17 and AZ33, which show elemental fractionation compatible with a separated steam phase, are located within the dominant-steam zone reported by Barragán et al. (2005) (Fig. 2B). Nieva et al. (1987b) calculated steam excesses in well AZ17 from 6 up to 43.5% of the total fluid volume, based on oxygen stable isotope enrichments. The strong elemental fractionation of Ne and Xe ($F(^{20}\text{Ne}) = 1.3$ and $F(^{132}\text{Xe}) = 0.79$) in this well (Table 3) and simulated curves at low temperatures suggests that steam excess reached values close to 100% of the total fluid.

Fig. 8A,B shows the R/Ra ratio not corrected for air contamination plotted against the $F(^{20}\text{Ne})$ and the $F(^{132}\text{Xe})$ values, respectively. The distribution of the measured values can be explained by fractionation of the atmospheric noble gases Ne, Kr and Xe by boiling and phase separation followed by massive air addition. Although low gas content at hot spring samples such as Tejamaniles and Araró north and east could result from air contamination during sampling, AZ2 air content appears to be ubiquitous to the well. Indeed, R/Ra values measured in duplicate at 1-year interval and using 2 different sampling devices are similar within error (R/Ra in 2007 = 2.79 ± 0.22 and R/Ra in 2009 = 2.63 ± 0.06 (2 σ); Table 3). It is worth noting that Barragán et al. (2005) clearly showed that well AZ2 is strongly affected by re-injected fluids (76% of the total discharged fluid). Injectate likely contains large amounts of dissolved air at either solubility equilibrium (ASW conditions) values or, more likely, as excess air. The amount of re-injected fluid in AZ2 can be roughly estimated by assuming a simple mixing between an ASGW fluid affected by boiling (e.g., Maritaro site 1; Fig. 8A,B) and air. Using measured $F(^{20}\text{Ne})$ values, we find that between 73 and 88.5% of the AZ2 fluid is injectate, while using $F(^{132}\text{Xe})$ values, the volume of re-injected brines increases from 89.6 to 96.6% of the total. These values suggest that after over 25 years of exploitation of fluids at Los Azufres, wells from the western border of the southern production zone (Fig. 2B) discharge almost entirely re-injected brines.

5.3. Origin of the CO_2 in the field

The main gas phase in Los Azufres reservoir is CO_2 , often accounting for over 96% of the total NCG (non-condensable gas) phase extracted from geothermal wells. Birkle et al. (2001) reported a few measured $\delta^{13}\text{C}$ data in CO_2 . Their $\delta^{13}\text{C}$ values ranged from -5.4% (vs. V-PDB) in well AZ5 to -19.5% in well AZ43. The higher value could be related to magmatic CO_2 ($\delta^{13}\text{C}$ from -8 to -6% ; Deines, 2002), but values down to -10% can only be explained by assuming a contamination with organic matter ($\delta^{13}\text{C} \leq -20\%$). Due to a lack of organic matter throughout the lithological reservoir column, the origin of extremely negative $\delta^{13}\text{C}$ values was explained by an organic input into the geothermal reservoir from meteoric water (Birkle et al., 2001). We re-analyzed $\delta^{13}\text{C}$ in several wells and hot springs of Los Azufres (Table 3) during our sampling campaigns, three of which (AZ9, AZ22 and AZ28) had been previously analyzed by Birkle et al. (2001). The $\delta^{13}\text{C}$ in AZ9 is $-6.9 \pm 0.12\%$ while Birkle et al. (2001) reported a value of -8.4% . Our measured $\delta^{13}\text{C}$ values in AZ22 and AZ28 are -7.2 ± 0.03 and $-7.6 \pm 0.01\%$, respectively, while corresponding values reported by Birkle et al. (2001) are -6.9% and -11.1% , respectively.

Except for Araró ($\delta^{13}\text{C} = -9.4 \pm 0.01\%$), all the analyzed CO_2 samples in this study show $\delta^{13}\text{C}$ values clustered around -7% , which is within the range assumed for mantle C. The C isotopic composition of the Araró hot spring is slightly lighter and could be explained by the presence of recent recharge water rich in organic matter. This is compatible with the δD and $\delta^{18}\text{O}$ isotopic composition of Araró, which clearly shows the influence of recent recharge (Fig. 5).

6. Conclusions

Noble gases, stable (δD , $\delta^{18}\text{O}$, $\delta^{13}\text{C}$) and radiogenic ($^{87}\text{Sr}/^{86}\text{Sr}$) isotopes were measured in several geothermal wells and hot springs of the Los Azufres geothermal field in central Mexico. Although studied for over 30 years, few noble gas isotopic data exist from this important geothermal field. The aim of this work is to provide additional information on fluid circulation in the field, and to assess current reservoir conditions at depth, following several decades of re-injection of used brines to increase the longevity of this field. Hot springs in the northern zone (Maritaro), an area less affected by re-injection (Birkle et al., 2001), display the highest $^3\text{He}/^4\text{He}$ ratio of 7 Ra, in the range of subcontinental mantle values (~ 6.5 ; Dunai and Baur, 1995). The lowest $^3\text{He}/^4\text{He}$ ratios

are measured at Araró hot springs in the northeast, outside of the caldera of Los Azufres. Helium isotopic composition of thermal waters is correlated with both $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Fig. 6) and stable isotopes of the water molecule (δD and $\delta^{18}\text{O}$). This suggests mixing between thermal fluids acquiring mantle He from deep parent magmas with possibly radiogenic Sr from basement rocks and groundwater discharged at Araró, which has likely circulated for an extended time within the andesitic reservoir of the caldera prior to discharging near Lake Cuitzeo. These waters acquired a more radiogenic He signature derived from the aging effect of older Miocene andesites. Interaction of water with the magmatic bodies at depth supplied most of the CO_2 that constitutes the main NCG phase of the field. Two wells (AZ13 and AZ62) in the southern zone of the field have radiogenic $^{40}\text{Ar}^*$ which suggests that an older crustal fluid might be locally present in the field. All other noble gases are atmospheric in origin, but their elemental composition is strongly fractionated by boiling and steam separation caused by years of used brine re-injection. The current noble gas signature leads us to suggest that the area affected by boiling in the northern productive zone has now further extended to the north with respect to that found in the previous sampling campaign, almost 10 years prior (Barragán et al., 2005). In the southern zone, fluids from well AZ2 are presently composed of 78 up to 96% of injectate. A large-scale noble gas survey in productive wells of Los Azufres would be helpful in precisely mapping these processes at depth and in providing an estimate of the declining enthalpy of the field.

Acknowledgments

We thank an anonymous reviewer and Matthijs Van Soest for their thoughtful reviews. We wish to thank Yuri Taran (UNAM), Gabriela Gómez and Ulises Oros (UMSNH-IIM) for their invaluable help during fieldwork. We also thank the direction of "Proyectos Geotermoelectricos de la CFE" and the "Residencia de Los Azufres" for assistance in the field. Philippe-Xavier Normandeau (McGill Un.) helped in measuring the C isotopes in Los Azufres fluids. This work was supported by the Ministry of International Relations of Québec (XI Québec-Mexico workshop contract no. 13667) as well as by NSERC Discovery Grants of AT (no. 105669) and DLP (no. 314496). Michelle Laithier (UQAM) is thanked for producing the artwork.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.jvolgeores.2012.09.006>.

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